

REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 12-03-2006		2. REPORT TYPE Conference Proceedings (non-refereed)			3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE An Evaluation of Ballast Tank Corrosion in Hypoxic Seawater				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER 0601153N		
				5d. PROJECT NUMBER		
6. AUTHOR(S) Lee, Jason S., Ray, Richard I., Little, Brenda J., Lemieux, Edward				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER 73-5052-15-5		
				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/PP/7303-05-6048		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Oceanography Division Stennis Space Center, MS 39529-5004				10. SPONSOR/MONITOR'S ACRONYM(S) ONR		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy St. Arlington, VA 22217-5660						
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution is unlimited.				20060605034		
13. SUPPLEMENTARY NOTES <i>U.S. Govt authors; ALL US Govt work; Not copyrighted</i>						
14. ABSTRACT Investigations were undertaken to evaluate the impact of hypoxia on corrosion within ballast tanks. Carbon steel coupons were exposed to seawater in alternating fill/drain conditions encountered in operational ballast tanks. The following alternating exposure conditions between fill/drain conditions were examined: 1) oxygenated seawater/air, 2) hypoxic seawater (0.2 mg/L O ₂)/hypoxic gas. The effect of oxygen on corrosion in a hypoxic environment was evaluated by introducing oxygenated air into the hypoxic chamber at the midpoint of the experiment. Differences in corrosion rate and morphology before and after the introduction of oxygen were quantified.						
15. SUBJECT TERMS carbon steel, seawater, ballast, deoxygenation, alternate immersion, SRB, sulfide						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT		18. NUMBER OF PAGES	
a. REPORT	b. ABSTRACT	c. THIS PAGE	UL		16	
Unclassified	Unclassified	Unclassified			19a. NAME OF RESPONSIBLE PERSON Jason S. Lee	
					19b. TELEPHONE NUMBER (Include area code) 228-688-4494	

PUBLICATION OR PRESENTATION RELEASE REQUEST

Pubkey: 4696

NRLINST 5600.2

1. REFERENCES AND ENCLOSURES	2. TYPE OF PUBLICATION OR PRESENTATION	3. ADMINISTRATIVE INFORMATION
Ref: (a) NRL Instruction 5600.2 (b) NRL Instruction 5510.40D	() Abstract only, published () Book (X) Conference Proceedings (refereed) () Invited speaker () Journal article (refereed) () Oral Presentation, published () Other, explain	STRN <u>NRL/PP/7303-05-6048</u> Route Sheet No. <u>7303/</u> Job Order No. <u>73-5052-15-5</u> Classification <u>X</u> U <u> </u> C Sponsor <u>ONR BASE</u> approval obtained <u> </u> yes <u>X</u> no
Encl: (1) Two copies of subject paper (or abstract)	() Abstract only, not published () Book chapter () Conference Proceedings (not refereed) () Multimedia report () Journal article (not refereed) () Oral Presentation, not published	

4. AUTHOR

Title of Paper or Presentation

An Evaluation of Ballast Tank Corrosion in Hypoxic Seawater

Author(s) Name(s) (First, MI, Last), Code, Affiliation if not NRL

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It is intended to offer this paper to the NACE Corrosion 2006

(Name of Conference)

12-MAR - 16-MAR-2006, San Diego, CA, Unclassified

(Date, Place and Classification of Conference)

and/or for publication in NACE Corrosion 2006, Unclassified

(Name and Classification of Publication)

(Name of Publisher)

After presentation or publication, pertinent publication/presentation data will be entered in the publications data base, in accordance with reference (a).


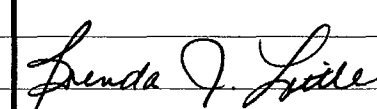
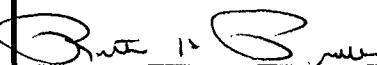
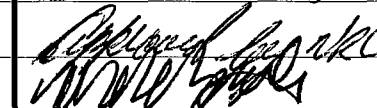
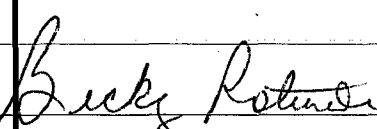
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5. ROUTING/APPROVAL

CODE	SIGNATURE	DATE	COMMENTS
Author(s) <u>Lee</u>		<u>11/2/05</u>	<u>Need by 22 Nov 05</u> <u>Publicly accessible</u> <u>sources used for</u> <u>this publication</u>
Section Head			
Branch Head Brenda J. Little, 7330		<u>11/02/05</u>	
Division Head			
Ruth H. Preller, 7300		<u>10/2/05</u>	1. Release of this paper is approved. 2. To the best knowledge of this Division, the subject matter of this paper (has <u> </u>) (has never <u>X</u>) been classified.
Security, Code 7030.1			
Office of Counsel, Code 1008.3		<u>11/8/05</u> <u>11/2/05</u>	1. Paper or abstract was released. 2. A copy is filed in this office. <u>SSC-4470</u>
ADOR/Director NCST E.O. Hartwig, 7000			
Public Affairs (Unclassified/ Unlimited Only), Code 7030.4		<u>11/4/05</u>	<u>ABSTRACT APPROVAL</u> <u>#5-1226-1603</u>
Division, Code			
Author, Code			

AN EVALUATION OF BALLAST TANK CORROSION IN HYPOXIC SEAWATER

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ABSTRACT

Investigations were undertaken to evaluate the impact of hypoxia on corrosion within ballast tanks. Carbon steel coupons were exposed to seawater in alternating fill/drain conditions encountered in operational ballast tanks. The following alternating exposure conditions between fill/drain conditions were examined: 1) oxygenated seawater/air, 2) hypoxic seawater (0.2 mg/L O₂)/hypoxic gas. The effect of oxygen on corrosion in a hypoxic environment was evaluated by introducing oxygenated air into the hypoxic chamber at the midpoint of the experiment. Differences in corrosion rate and morphology before and after the introduction of oxygen were quantified.

KEY WORDS: carbon steel, seawater, ballast, deoxygenation, alternate immersion, SRB, sulfide

INTRODUCTION

Deoxygenation of seawater has been demonstrated as an environmentally friendly ballast water treatment to control introduction of non-native aquatic species.¹ Investigators have proposed that the same treatment provides a low-cost, effective corrosion control measure for uncoated carbon steel ballast tanks based on the concept that reducing oxygen from the ballast tanks will limit oxidation.^{1, 2} Matsuda *et al.*² conducted shipboard trials by sealing a ballast tank at the deck and installing vertical pipes into the headspace. They reported that pumping pure nitrogen gas into the headspace for 1.5 hr reduced dissolved oxygen (DO) levels in the seawater to approximately 0.2 parts-per-million (ppm) and decreased the rate of uniform corrosion of carbon steel by 90% as determined by weight loss. Lee *et al.*^{3, 4} attempted to reproduce the experimental conditions described by Matsuda in the laboratory with fully instrumented chambers, containing carbon steel electrodes and monitoring DO and instantaneous corrosion rates. They were able to produce hypoxic (< 0.2 ppm O₂) seawater by injecting inert gases (containing 0.2 ppm O₂) into natural seawater. However, because of oxygen consumption by corrosion reactions and microbial respiration, the hypoxic seawater became anaerobic (DO ~0.0 ppm) within the first hours of the experiment. The laboratory experiments compared corrosion resulting from stagnant

aerobic natural seawater with corrosion resulting from stagnant anaerobic natural seawater over a one-year period. They demonstrated the following: (1) corrosion was more aggressive under totally anaerobic conditions as measured by instantaneous corrosion rates ($1/R_p$) and weight loss, (2) under aerobic conditions corrosion was uniform and the surface was covered with iron oxides (lepidocrocite and goethite) and (3) under anaerobic conditions the corrosion was localized pitting and the corrosion products were mackinawite and pyrrhotite. In addition, introduction of oxygen to the totally anaerobic stagnant tank caused an immediate increase in weight loss and an order-of-magnitude higher instantaneous corrosion rate.

In a separate series of experiments Lee *et al.*⁵ attempted more complex field experiments in which chambers were filled and drained, a typical operating circumstance for ballast tanks. The exposure conditions were designed for the following regimes: (1) fill/drain cycles of alternating natural oxygenated seawater and air (aerobic/aerobic), (2) fill/drain cycles alternating hypoxic natural seawater and air (deoxygenated/aerobic) and (3) fill/drain cycles alternating hypoxic natural seawater and inert gas (0.2 ppm DO) (deoxygenated/deoxygenated). The field experiments demonstrated decreased corrosion in deoxygenated seawaters using linear polarization measurements. They also demonstrated the difficulty of maintaining hypoxic DO levels in seawater. In addition to aerobic respiration and corrosion reactions consuming oxygen, leaking gaskets and seals failed inadvertently introducing oxygen. When the seawater contained any oxygen, the impact of oxygen ingress on corrosion depended on the concentration of oxygen in the system at the time of introduction. Carbon steel exposed to cycles of hypoxic seawater and oxygenated atmosphere had higher corrosion rates than coupons exposed to cycles of either consistently aerobic or deoxygenated conditions.

The predominant corrosion mechanism for carbon steel in anaerobic seawater is sulfide-induced corrosion resulting from the presence and activities of sulfate-reducing bacteria (SRB). Seawater typically contains 2 g/L sulfate. SRB survive in oxygenated seawater, but reduce sulfate in anaerobic conditions. Anaerobic conditions and sulfides can form within marine biofilms at biofilm/metal interfaces, independent of bulk oxygen concentrations.⁶ Several investigators⁷⁻⁹ have suggested that the most corrosive operating condition for carbon steel in seawater is one in which carbon steel is exposed to alternating oxygenated/deoxygenated seawater. Under constant oxygenation an oxide will form that provides corrosion resistance. Under anaerobic conditions, naturally occurring SRB produce sulfides, resulting in conversion of the oxide to a sulfide. The result of repeated oxygenated/deoxygenated cycles is reportedly severe localized corrosion, *i.e.*, pitting. Hamilton¹⁰ proposed a model for microbiologically influenced corrosion (MIC) in which he concluded that all mechanisms involved a process of electron transfers from base metal to oxygen as the ultimate electron acceptor through a series of coupled reactions. The specific coupled reactions varied with mechanism and causative organism. In the case of SRB, sulfate, an intermediate electron acceptor, is reduced to sulfide that reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. Consistent with that model, most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium.^{6, 11}

Despite the understanding gained from the previous laboratory and field experiments, Lee *et al.*⁵ did not maintain the hypoxic condition (< 0.2 ppm O_2) specified by Tamburri *et al.* as essential to prevent growth of non-native invasive aquatic species and control corrosion. The justification for that precise concentration, established in the Matsuda experiments is not clear to the present authors. Tamburri *et al.* used a Venturi Oxygen Stripping^{TM(1)} technique to produce hypoxic seawater. They reported a greater than 90% mortality of Chesapeake Bay zooplankton in less than 48 hours in seawater

¹ Trademark of N.E.I. Treatments Systems, LLC, Los Angeles, CA

containing 0.26 – 0.87 ppm oxygen. Despite the increased organics in seawater after oxygen stripping due to dead phytoplankton, they reported essentially no change in the total bacterial population over 96 hours as compared to untreated controls. They do not include a description of the method used to determine bacterial population. In the laboratory and field experiments Lee *et al.* followed specific groups of bacteria – SRB, acid-producing bacteria (APB), general aerobes and general anaerobes. They found that the total number of bacteria do not change with exposure condition (aerobic vs. anaerobic). However, the number of organisms within the specific groups fluctuated markedly with exposure condition. For example, SRB could not be measured in freshly collected seawater, but after 48 days, in the totally anacrobic exposure, a population of 10^3 cells/ml was measured.

In this paper the corrosion of unprotected carbon steel was evaluated in following alternating fill (14 days)/drain (14 days) exposure conditions: 1) oxygenated seawater/air, 2) hypoxic seawater/inert gas (0.2 ppm DO). The experiments described in this paper were designed to maintain a precise hypoxic oxygen level (0.2 ppm), meaning that oxygen could be added or removed, depending on the reactions within the chamber and leaks in the seals. As in previous experiments, dissolved oxygen and instantaneous corrosion rates were monitored continuously in both chambers. Specific groups of bacteria were evaluated periodically. The impact of oxygen ingress on corrosion of carbon steel previously maintained in a hypoxic environment was evaluated to simulate a ship entering port and opening the ballast tank to drain or clean.

MATERIALS AND METHODS

Two identical chambers were built to expose 1020 carbon steel to natural and hypoxic Key West seawater (Figure 1a) for 396 days. Detailed description of this setup has been published previously³⁻⁵. Cylindrical chambers (35.5 cm dia. and 27.9 cm ht.) were constructed from heavy gauge, chemical resistant, opaque polyethylene. Corrosion coupons were descaled, non-polished 1020 carbon steel (Table 1), 1.5 cm dia. x 0.16 cm thick with an as-mill finish. Individual insulated wires were attached to the back of each pre-weighed coupon and held in place using conductive silver adhesive and carbon tape. The exposure side of the coupon was coated with vacuum grease and centered face down inside a plastic mount (3.175 cm dia. x 2.54 cm ht.). Coupons were mounted in epoxy with the wire connection exposed to the epoxy. Vacuum grease prevented intrusion of epoxy between the coupon face and the bottom of the mount and allowed the as-mill finish to be preserved. Epoxy-mounted carbon steel coupons were oriented in rows both vertically (12 coupons) and horizontally (6 coupons) in each chamber to simulate ballast tank sidewalls and bottoms, respectively, for a total of 18 coupons (Figure 1b). A heavy gauge plastic cylinder (17 cm dia. x 23 cm ht.) held the coupons in place with the vertically oriented coupons positioned inwards and the horizontally oriented coupons positioned upwards. Prior to seawater exposure, coupons were rinsed in acetone, ethanol and distilled water and dried with nitrogen gas to removed vacuum grease and residual surface debris. Ag/AgCl electrodes and a platinum/niobium mesh were used as reference and counter electrodes, respectively (Figure 1a). The counter electrode mesh was 225 cm² in area (15 cm x 15 cm) with a cylindrical shape to maximize current distribution to all sample electrodes.

Experiments were conducted with natural seawater at the Naval Research Corrosion Laboratory, Key West, FL. Coupons in the chambers were exposed to the following conditions: (1) 14 day fill/14 day drain cycles of alternating natural oxygenated seawater and air – designated aerobic, (2) 14 day fill/14 day drain cycles alternating hypoxic seawater and gas – designated hypoxic. During the fill cycle, the water line was at the same level as row 2, whereas after draining a thin layer of seawater remained in the bottom of both chambers preventing row 4 coupons from desiccating (Figure 1b). No coupons were placed in the row 2 position. Coupons in row 1 were employed to determine the effect of

salt spray on the corrosion of C1020 above the water line during the fill condition. DO levels in natural Key West, FL seawater were decreased using an in-line injection of premixed gases containing 0.2 ppm DO. A combination of carbon dioxide (CO₂) and nitrogen (N₂) gases was used to decrease gas bubble size, thereby increasing the bubble surface-to-volume ratio and facilitating DO removal to the target level of 0.2 ppm. The system was designed so that the hypoxic gas was also used to blanket the headspace in the hypoxic exposure during the fill cycle or the entire chamber volume during the drain cycle. In previous experiments⁵, preventing inadvertent introduction of oxygen into hypoxic conditions was a significant engineering design problem. To mitigate this problem a pressure sensor was used to keep a positive pressure of the gas mixture within the hypoxic chamber at all times. When the pressure in the hypoxic tank dropped below 1.005 atm, a solenoid valve opened to allow hypoxic gas to repressurize the chamber.

After 101 days exposure, comprised of 4 fill cycles and 3 drain cycles, both chambers were opened and 3 coupons from each row were removed. Coupons from rows 3 and 4 were placed in sealed containers with water from their corresponding chamber. Coupons from row 1 were wrapped in tissue paper and placed in a sealed plastic bag with either air (aerobic) or an anaerobic gas pack (hypoxic). All removed coupons were transported to the Naval Research Laboratory, Stennis Space Center, MS for analysis. Both chambers were drained and opened to air for 14 days. The pressure sensor in the hypoxic chamber was deactivated during this 14-day period. After the 14-day air exposure, each chamber was filled with seawater matching the conditions prior to air exposure. (It should be noted that the 14-day air exposure in the oxygenated case was no different than any of the other drain cycles in the oxygenated condition.) Then 4 fill/3 drain cycles were repeated. At the time of writing this technical paper, the experiment still has 1 drain/fill cycle to complete. At the conclusion of the cycle the remaining coupons will be removed and examined as described below.

Coupons were fixed in 4% glutaraldehyde in seawater, rinsed in distilled water and examined to assess the extent of biofilm formation and corrosion morphology. Environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) were used to characterize the corrosion morphology, biofilm structure and corrosion product composition on the metal surface.¹² After ESEM evaluation, coupons were acid-cleaned¹³, weighed for weight loss and re-examined. Linear polarization resistance (LPR) was performed on each coupon weekly during a fill cycle. LPR was used to determine the polarization resistance (R_p) of each coupon. The inverse ($1/R_p$) is the instantaneous corrosion rate given in (ohms⁻¹). Corrosion rate was not converted into penetration rate, by way of the Stern-Geary relationship and Faraday's Law,¹⁴⁻¹⁶ due to the lack of anodic and cathodic Tafel slopes recorded during this examination. Acquisition time for R_p is <1 min. DO in each chamber was monitored continuously using 2 DO electrodes and 2 mini data loggers. One DO electrode was placed in the headspace above the row 1 position while the other DO electrode was placed at the row 4 position, below the drain cycle water line. This arrangement allowed DO to be measured in the chamber atmosphere and seawater during both drain and fill conditions.

Water samples from the midsections of each chamber were collected after 100 days exposure (25 days since last drain cycle). The following parameters were measured using standard techniques: bulk pH, sulfide and sulfate concentrations, and salinity. Sulfide concentrations were determined in triplicate using the methylene blue method 228 C¹⁷ and a spectrophotometer. A sterile 5 ml syringe was used to collect 4 ml from the water sample. One ml was used to inoculate serial dilutions (10^5) of each of the following seawater media: phenol red dextrose broth, Postgate medium B, nutrient broth and thioglycollate medium used to determine most probable numbers of APB, SRB, general heterotrophic aerobes, and anaerobes, respectively. Dilutions were incubated for 28 days at room temperature.

RESULTS & DISCUSSION

Water Analysis

Prior to deliberate introduction of atmospheric oxygen at 101 days, chemistry and bacterial populations from both oxygenated and hypoxic chambers, as well as natural Key West seawater, were examined and are reported in Tables 2 and 3, respectively. The chamber waters had been stagnant for 25 days at the time of collection. Natural seawater had a pH of 7.66 while the oxygenated water had a slightly higher pH of 7.84 after 25 days of stagnation. Hypoxic water had a lower pH of 6.47 due to CO_2 in the process gas mixture dissolving into the water. Sulfide concentration was negligible (in the parts-per-billion range) in the natural seawater. Hypoxic water had the highest sulfide concentration (0.36 ppm) and oxygenated water having 0.14 ppm. Natural seawater had sulfate concentration of 3864 ppm, comparable to previously reported values.³⁻⁵ Both natural and hypoxic seawaters had salinities of 35 ppt. Oxygenated seawater salinity was higher (36 ppt) due to evaporation of water via the open port to air. Culturable bacterial counts of the seawaters, as shown in Table 3, indicate that natural seawater had high concentrations of aerobes, general anaerobes, APB, and SRB. Bacterial counts were less for all groups after a 25-day stagnation period in both oxygenated and hypoxic chambers. Notably, no culturable SRB were identified in either chamber.

Dissolved Oxygen Levels

Dissolved oxygen measurements were made throughout the experiment during both the fill and drain cycles, as shown in Figure 2, where shaded regions indicate drain cycles. In the oxygenated chamber, the headspace DO level remained between 6.5 and 5.5 ppm and was unaffected by cycling water levels. This effect was expected since the oxygenated chamber was open to air at all times. DO level in the bottom of oxygenated tank ranged between 2 and 4.5 ppm with an average of about 3.5 ppm. Spikes in DO levels correspond to drain cycles where the water level dropped below the DO electrode, exposing it to atmospheric DO levels. In the hypoxic chamber, DO levels in both the headspace and bottom of ranged between <0.1 and 2.5 ppm and were significantly influenced by cycling. At the onset of draining the DO level spiked to as high as 2.5 ppm. DO levels returned to hypoxic design value of 0.2 ppm after 5 days from hypoxic gas pressurizing the chamber, and oxygen depletion due to corrosion reactions and bacterial respiration.⁵ Fill cycle onsets had less effect on DO levels in the hypoxic chamber with DO level peak at 0.7 ppm. At 101 days exposure, oxygenated and hypoxic chambers were opened to air during a drain cycle. DO levels in both headspaces and bottoms were the same, 6.0 ppm and 3.5 ppm, respectively. This intentional introduction of oxygen was meant to simulate a ship entering port with the hypoxic gas system deactivated and the ballast tank opened to air and drained for cleaning. After 115 days the hypoxic gas pressurization system was reactivated and the chamber was refilled to simulate a ship returning to duty.

Linear Polarization Resistance

Instantaneous corrosion rates ($1/R_p$ reported in units of ohms^{-1}) were measured using the LPR technique weekly on electrodes in rows 3 (side) and 4 (bottom) in each chamber and are reported as average values in Figure 3. As in Figure 2, shaded regions indicate drain cycle periods. Due to technical difficulties, $1/R_p$ data after the initial measurements and up to 75 days exposure were not recorded. Initially, all coupons had low corrosion rates in the range of 0.0015 – 0.0025 ohms^{-1} . At 75 days, coupons still indicated the same low instantaneous corrosion rates except for the side coupons in the oxygenated chamber which corroded at an average rate of 0.048 ohms^{-1} . At 83 days the rate had

jumped to over 0.07 ohms^{-1} . After opening, both tanks were drained and exposed to air (101 days) and refilled with their respective oxygenated or hypoxic seawaters. Instantaneous corrosion rates for both side and bottom coupons in the hypoxic chamber jumped to $\sim 0.04 \text{ ohms}^{-1}$. Corrosion rate of bottom coupons in the oxygenated chamber remained low (0.0025 ohms^{-1}) while the side coupons still had a corrosion rate of over 0.06 ohms^{-1} . Instantaneous corrosion rates decreased over the next 60 days in all cases except the oxygenated bottom which increased by 2x, but still an order-of-magnitude below the oxygenated side corrosion rate.

Weight Loss

Weight loss has been plotted as a function of placement in both oxygenated and hypoxic chambers in Figure 4. Coupons were removed from their respective chambers prior to intentional exposure to air at 101 days. The largest weight loss was measured for the oxygenated side coupons with an average value of 0.219 g. These data agree with the LPR measurements that also indicated the oxygenated side coupons had the highest corrosion rates. In comparison, side coupons in the hypoxic chamber had weight loss of less than 0.1 g. Bottom coupons had weight loss values less than corresponding side coupons. Oxygenated bottom coupons lost an average of 0.098 g, while coupons in hypoxic seawater lost an average of 0.040 g. Headspace coupons in both chambers had the lowest weight loss values. Oxygenated headspace coupons showed the lowest weight loss with an average value of 0.018 g, while hypoxic coupons lost an average of 0.029 g.

Corrosion Products and Morphology

Coupons were examined using optical microscopy and ESEM. The specific appearance of the coupons varied with placement and orientation within the chambers and representative coupons for both oxygenated and hypoxic exposure conditions are shown in Figures 5 and 6, respectively. As indicated in Figure 5, coupons from the oxygenated headspace had a reddish-orange corrosion product over roughly 70% of its surface. Beneath this corrosion product was a tenacious dark brown corrosion product. Side coupons had a very fragile reddish-orange corrosion product that easily sloughed to reveal a dark gray corrosion product underneath. Bottom coupons were covered by the reddish-orange corrosion product on less than 10 % of its surfaces with the rest of the surface being covered by dark grey corrosion products. Although crystal structure was not determined, the oxygenated corrosion products for similar exposures were a mixture of goethite and lepidocrocite.³⁻⁵ No sulfur was detected in any of the oxygenated corrosion products and encrusted bacteria were only found in the side and bottom coupon corrosion products that were directly exposed to seawater.

Coupons from the hypoxic chamber had corrosion products which varied by position and orientation as indicated in Figure 6. The headspace coupon was covered with dark red, flaky corrosion products with dark tubercles scattered across the surface. No sulfur was detected. Under high magnification, the corrosion products were made of fine structures with no evidence of encrusted bacteria. Side and bottom coupons had a two-tiered corrosion product consisting of an outer dark yellow layer which was easily removed and a tenacious dark gray corrosion product underneath. As in the case with the oxygenated coupons, corrosion product crystal structure was not determined but similar conditions from previously studies produced maghemite as a corrosion product.⁵ Under high magnification encrusted bacteria were found in both side and bottom coupons. Sulfur was also detected in the corrosion products with side coupons having 1 % S and bottom coupons having 3 % S. Notably, the bottom coupon had a very dense collection of bacteria on its surface (Figure 6, bottom right panel).

Prior to acid cleaning, the appearance of the coupons gave no indications of the type, severity or distribution of the corrosion (Figures 5 and 6). All coupons had some degree of general corrosion. Localized corrosion in the form of pitting was found only on oxygenated side coupons and headspace hypoxic coupons (Figure 7). Figure 7a shows the corrosion morphology of the oxygenated side coupons after acid cleaning. The surface had large diameter ($>250\text{ }\mu\text{m}$) pits over its surface with penetrations in excess of $400\text{ }\mu\text{m}$. The large amount of material degradation in this case also is reflected in the high corrosion rates determined by LPR and weight loss measurements. Side coupons maintained in hypoxic seawater had very uniform corrosion morphology (not shown). Figure 7b indicates pitting in the hypoxic headspace coupon from Figure 6. Pit size and distribution matches the spatial placement of the dark tubercles mentioned previously. In contrast, the oxygenated headspace coupon was only lightly etched. These findings are supported by the weight loss data which indicate more corrosion occurred in the hypoxic headspace compared to the oxygenated headspace. Bottom coupons from both chambers indicated only uniform corrosion.

CONCLUSIONS

- Introduction of oxygen into an anaerobic/hypoxic system resulted in an increase in corrosion rate and severity.
- The experiment is ongoing. However, after 101 days it is clear that deoxygenating seawater to produce a hypoxic environment produces a change in water chemistry, microbiology and the corrosion mechanism for unprotected carbon steel.
- Any benefit of deoxygenation to reducing corrosion rate is lost when oxygen is introduced.

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research Program element 0601153N (6.1 Research Program). NRL Publication Number NRL/PP/7303-05-6048.

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TABLES

Table 1. Chemical composition of carbon steel 1020.

AISI-SAE designation	C	Mn	P max	S max	Fe
1020	0.17-0.23	0.3-0.6	0.04	0.05	balance

Table 2. Seawater chemistry.

Exposure Condition	pH	S ²⁻ (ppm)	SO ₄ ²⁻ (ppm)	Salinity (ppt)
Natural Seawater	7.66	0.08	3864	35
Oxygenated (25 days stagnant)	7.84	0.14	-	36
Hypoxic (25 days stagnant)	6.47	0.36	-	35

Table 3. Bacterial counts.

Exposure Condition	Aerobes (10 ^x)	Anaerobes (10 ^x)	APB (10 ^x)	SRB (10 ^x)
Natural Seawater	5	4	5	4
Aerobic (25 days stagnant)	5	3	2	0
Hypoxic (25 days stagnant)	4	3	2	0

FIGURES

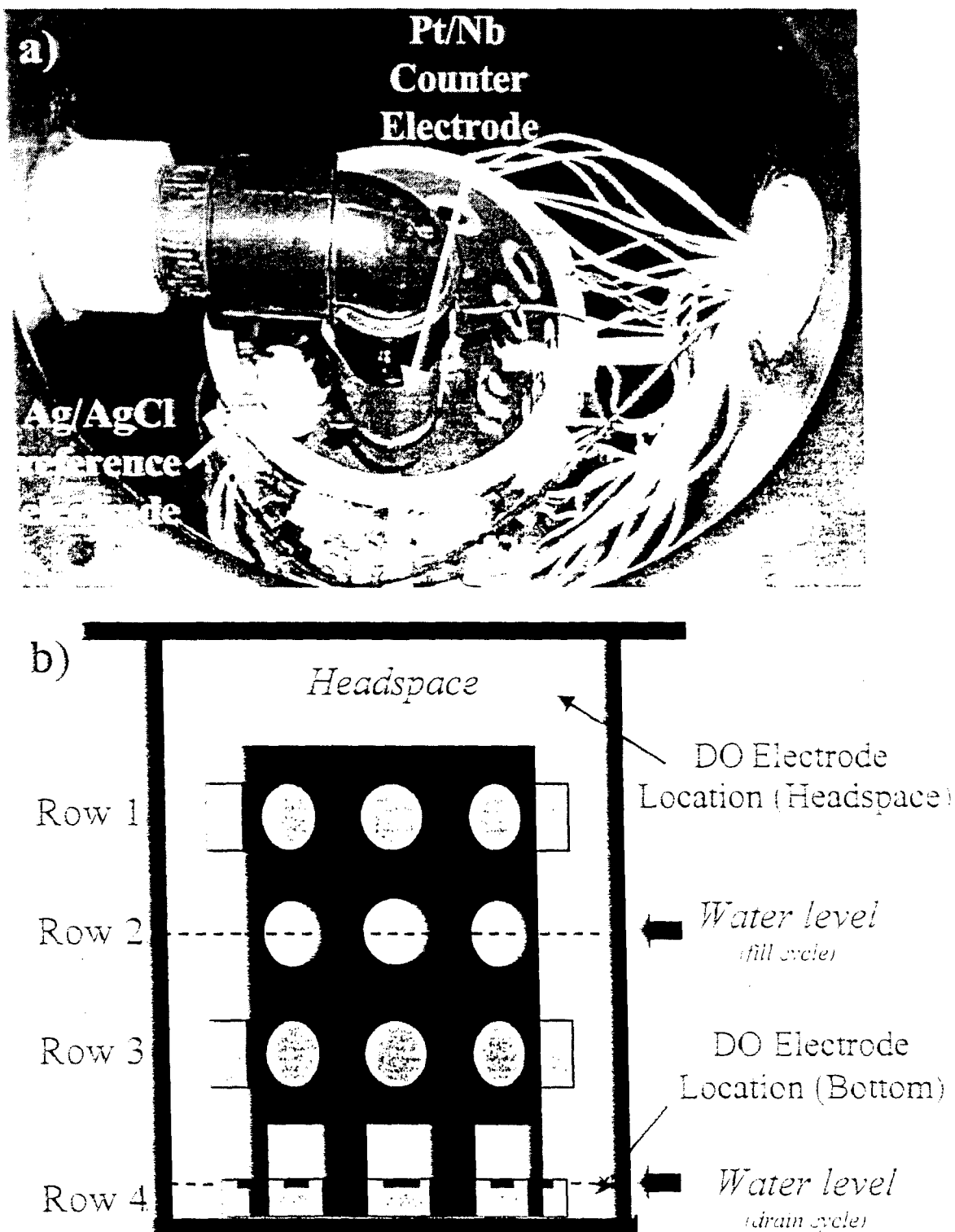


Figure 1. a) Experimental tank used to examine rates and mechanism of corrosion under oxygenated and hypoxic conditions. b) Schematic of coupon holder.

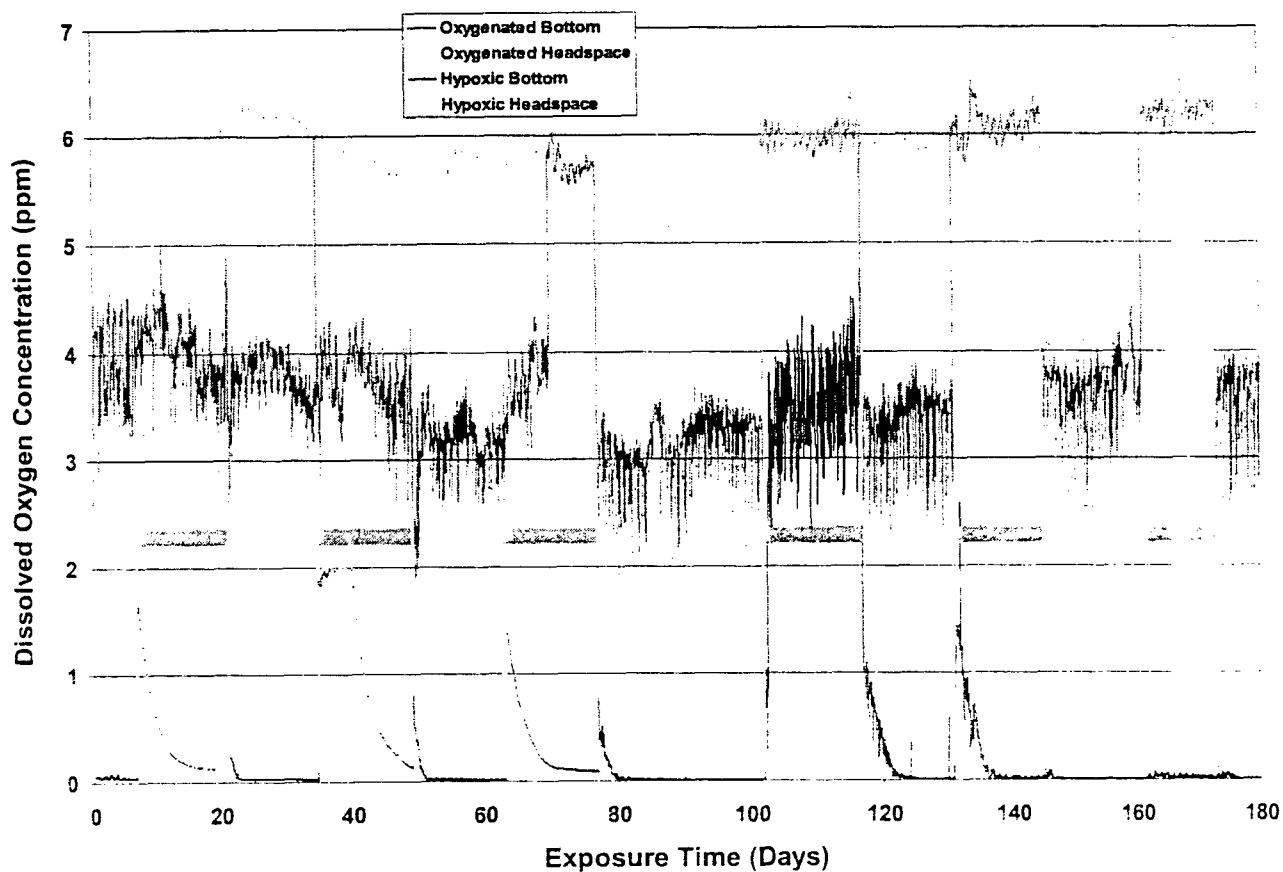


Figure 2. Dissolved oxygen concentration (ppm) measured in the headspace and bottom of both oxygenated and hypoxic chambers during fill/drain cycles. During one drain cycle starting (101 – 115 days exposure), both chambers were exposed to air. Shaded areas indicate drain cycle periods.

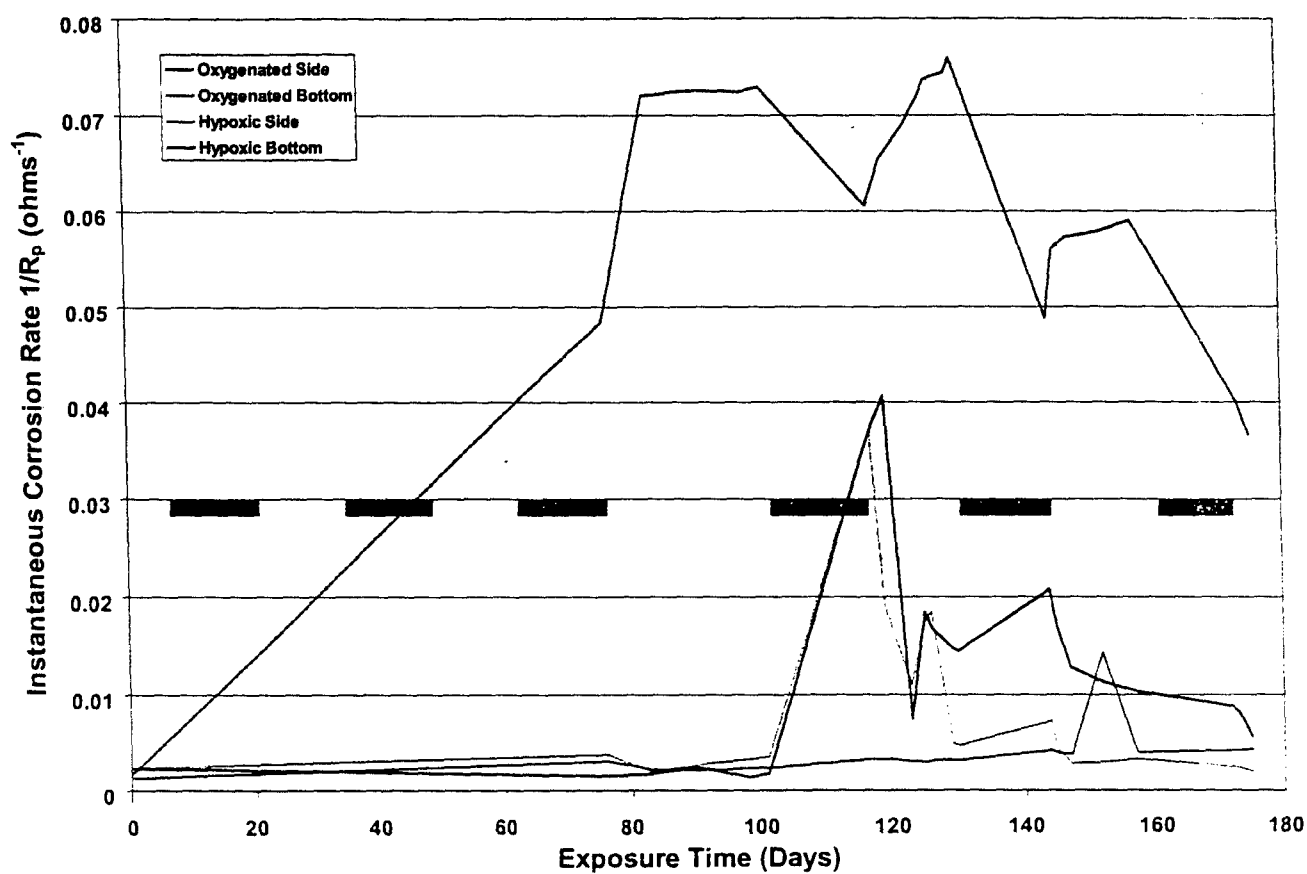


Figure 3. Average instantaneous corrosion rates ($1/R_p$ ohms^{-1}) of side and bottom coupons exposed to oxygenated and hypoxic seawaters. Shaded areas indicate drain cycle periods.

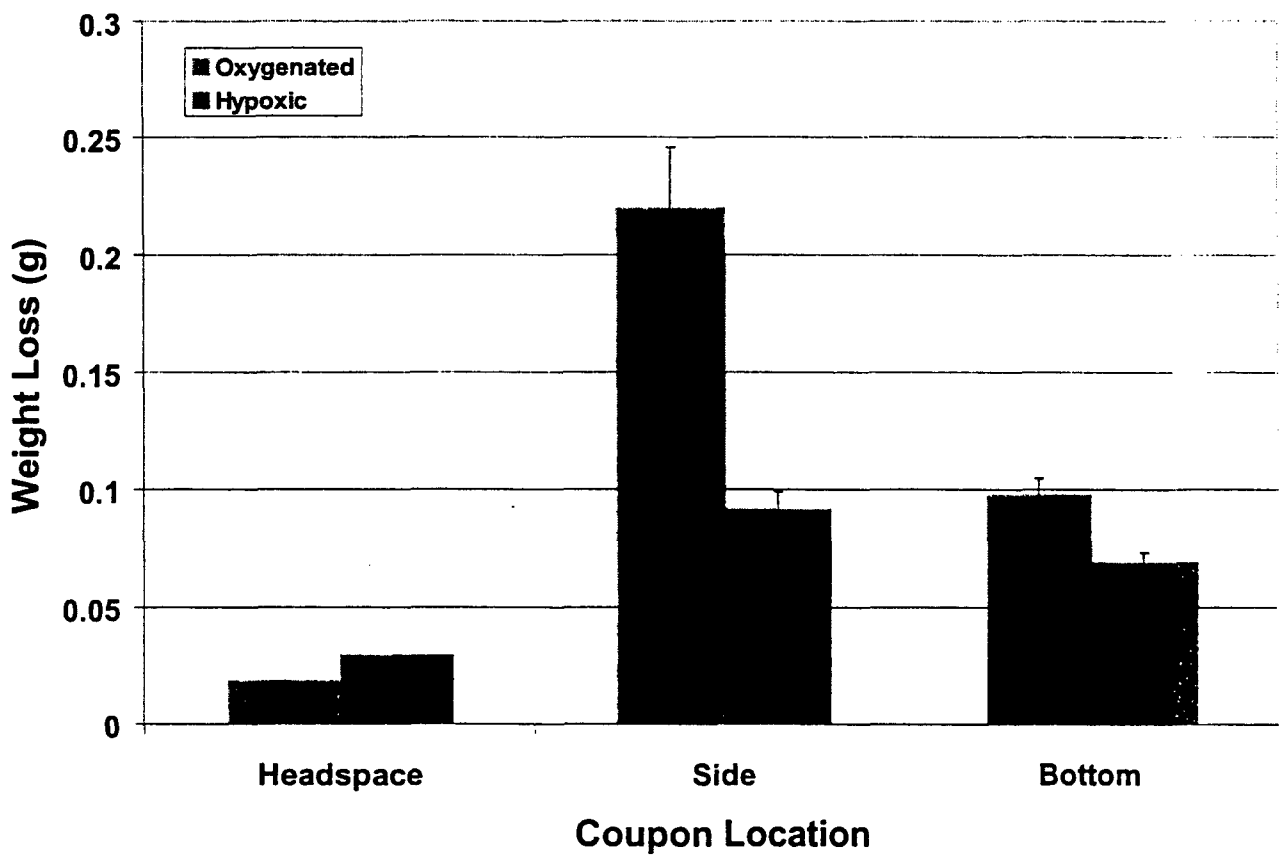


Figure 4. Weight loss (grams) of coupons after 101 days exposure to fill/drain cycling of oxygenated and hypoxic seawaters sorted by coupon location.

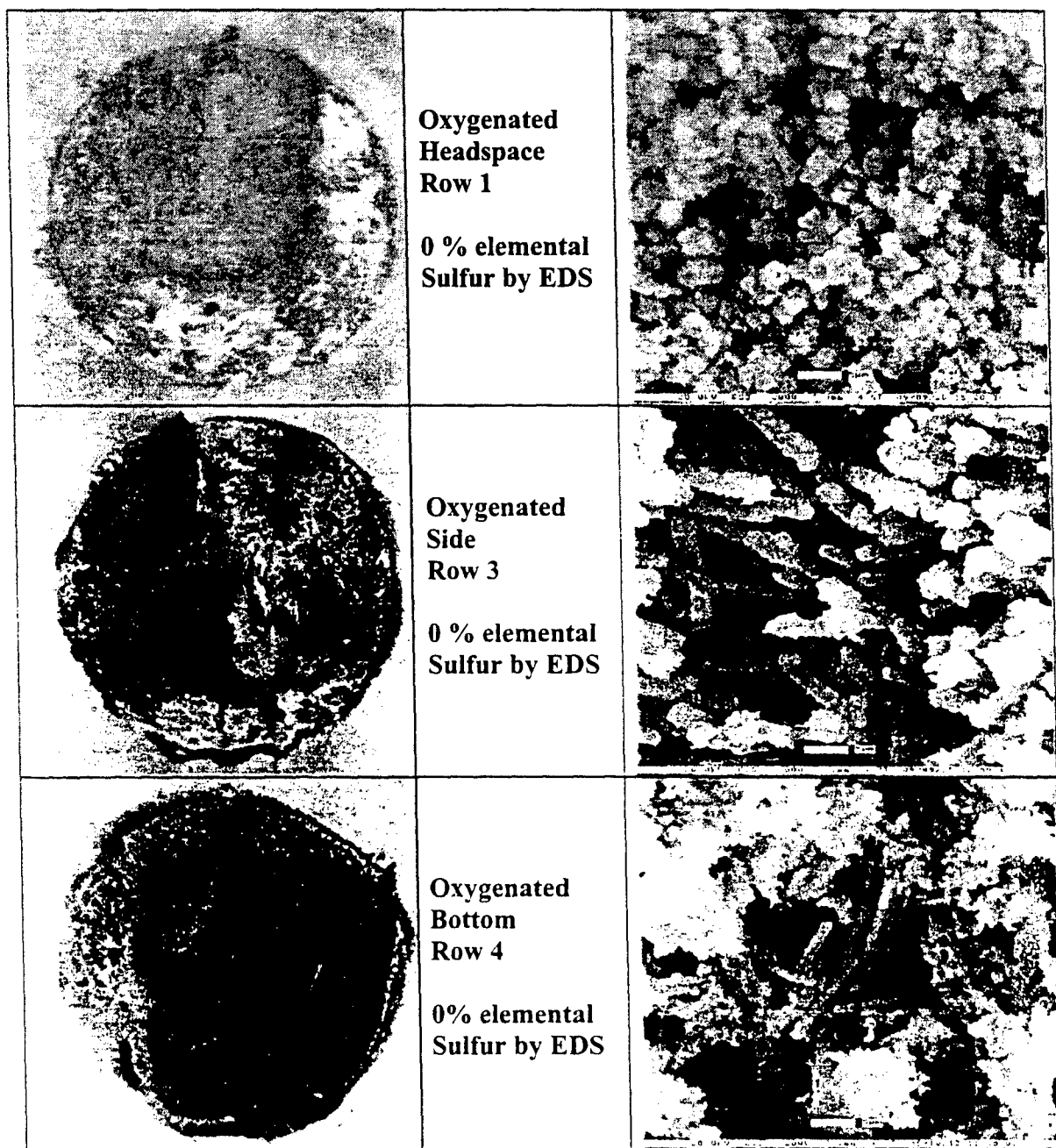


Figure 5. Photographs of coupons exposed to oxygenated seawater fill/drain cycling after 101 days. Micrographs of corrosion products from all three coupon locations within the chamber. No sulfur was detected in the corrosion products.

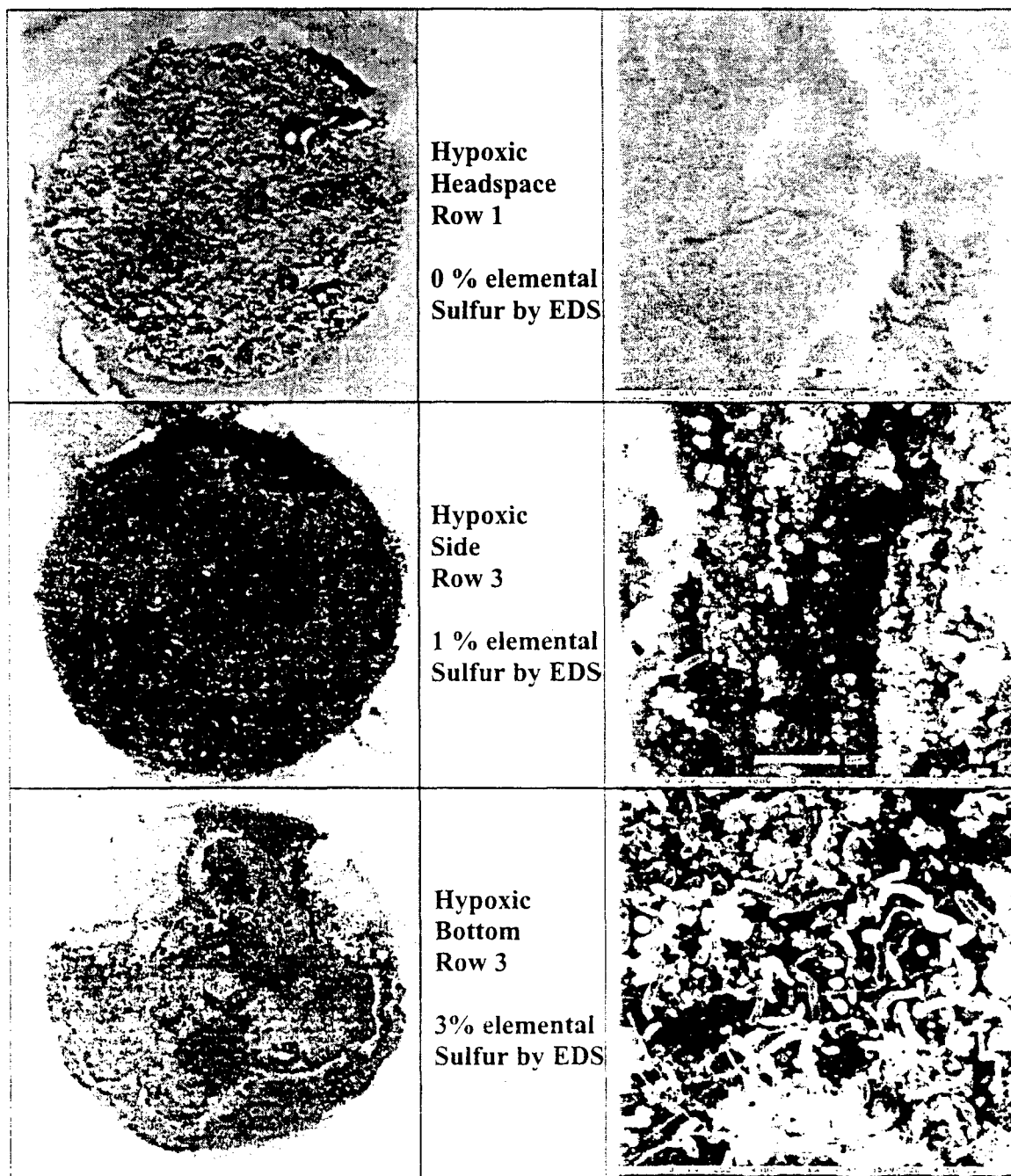


Figure 6. Photographs of coupons exposed to hypoxic seawater fill/drain cycling after 101 days. Micrographs of corrosion products from all three coupon locations within the chamber. Sulfur was detected in corrosion products from side and bottom coupons which were exposed directly to hypoxic seawater with large numbers of bacteria associated with the corrosion products.

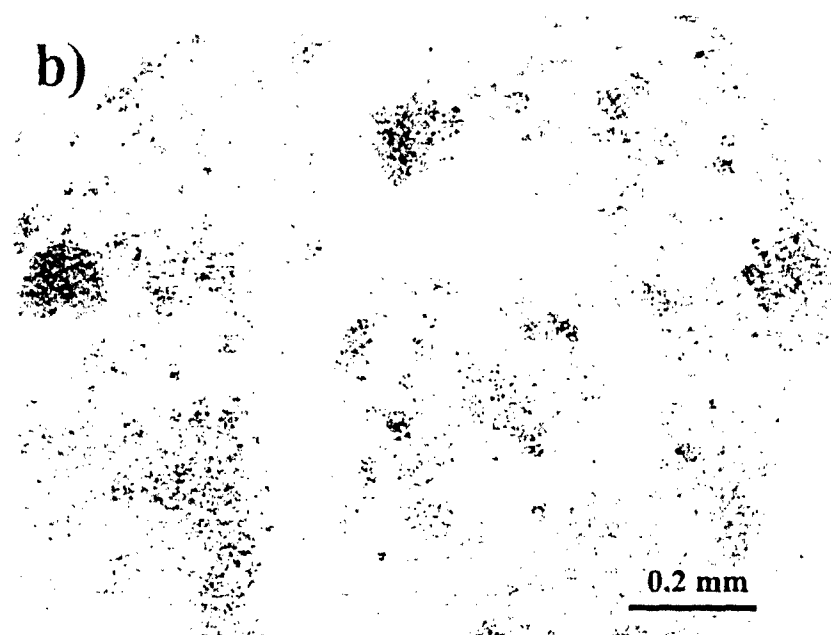
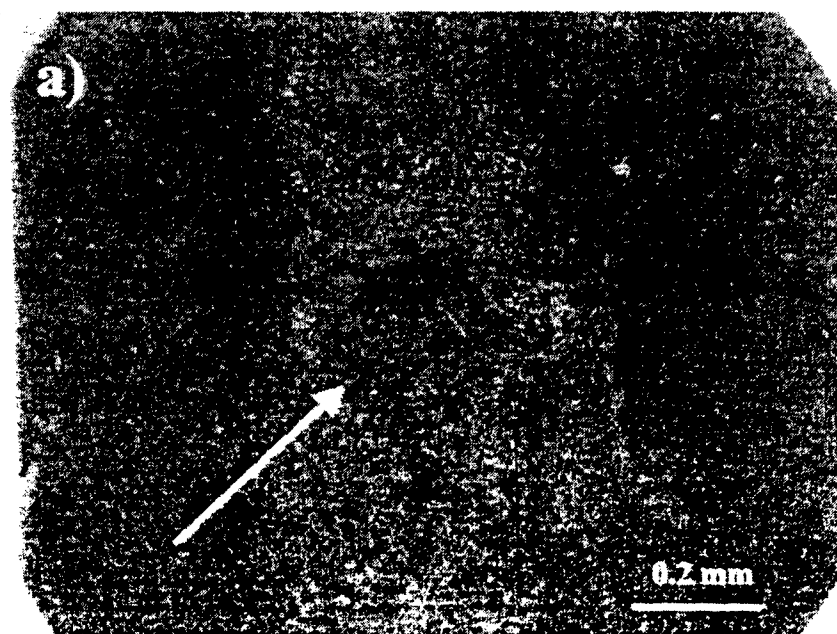


Figure 7. Corrosion morphology of coupons after acid cleaning. a) Photograph of side coupon exposed to oxygenated seawater indicating deep penetration into metal surface from localized corrosion. b) Photograph of headspace coupon from hypoxic chamber illustrating the presence localized corrosion.